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5-[[*(E)*-2-(4-Iodophenyl)hydrazinylidene]methyl]thiophene-2-carbaldehydeSolange M. S. V. Wardell,^a Geraldo M. de Lima,^b
Edward R. T. Tiekink^{c*} and James L. Wardell^{d‡}^aCHEMSOL, 1 Harcourt Road, Aberdeen AB15 5NY, Scotland, ^bDepartamento de Química, ICEx, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, MG, Brazil, ^cDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and ^dCentro de Desenvolvimento Tecnológico em Saúde (CDTS), Fundação Oswaldo Cruz (FIOCRUZ), Casa Amarela, Campus de Manguinhos, Av. Brasil 4365, 21040-900 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: edward.tiekink@gmail.com

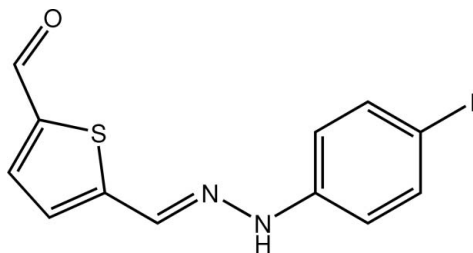
Received 17 December 2009; accepted 22 December 2009

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.058; wR factor = 0.113; data-to-parameter ratio = 16.6.

The title compound, $\text{C}_{12}\text{H}_9\text{IN}_2\text{OS}$, has an overall U-shape, with a dihedral angle of $21.4(3)^\circ$ between the thiophene and benzene rings. In the crystal, supramolecular chains mediated by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are formed along the b -axis direction.

Related literature

For background to 2-substituted thiophenes, see: Campaigne (1984); Kleemann *et al.* (2006). For the antimycobacterial activity of 2-substituted thiophenes, see: Lourenço *et al.* (2007). For a related structure, see: Ferreira *et al.* (2009). For background to the production of mono-hydrazones by the reaction of arylhydrazines with arenedicarbaldehydes, see: Reuch & Heflet (1956); Vaysse & Pastour (1964); Butler *et al.* (1990); Glidewell *et al.* (2005); Low *et al.* (2006); Wardell *et al.* (2006).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_9\text{IN}_2\text{OS}$ $M_r = 356.17$

‡ Additional correspondence author, e-mail: j.wardell@abdn.ac.uk.

Orthorhombic, *Pbca* $a = 6.9291(9)$ Å
 $b = 11.7602(10)$ Å
 $c = 30.958(4)$ Å
 $V = 2522.7(5)$ Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 2.69$ mm⁻¹ $T = 120$ K $0.16 \times 0.08 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2007)
 $T_{\min} = 0.616$, $T_{\max} = 0.746$ 15735 measured reflections
2614 independent reflections
1674 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.095$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.058$ $wR(F^2) = 0.113$ $S = 1.04$

2614 reflections

157 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 1.08$ e Å⁻³ $\Delta\rho_{\min} = -0.60$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1n}\cdots\text{O1}^i$	0.88 (4)	2.05 (5)	2.916 (8)	172 (5)

Symmetry code: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The use of the EPSRC X-ray crystallographic service at the University of Southampton, England and the valuable assistance of the staff there is gratefully acknowledged. JLW acknowledges support from CAPES and FAPEMIG (Brazil).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5284).

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supplementary materials

Acta Cryst. (2010). E66, o271-o272 [doi:10.1107/S1600536809055172]

5-*[(E)-2-(4-Iodophenyl)hydrazinylidene]methyl*thiophene-2-carbaldehyde

S. M. S. V. Wardell, G. M. de Lima, E. R. T. Tiekink and J. L. Wardell

Comment

The various uses of 2-substituted thiophenes have been well documented (Campaigne, 1984; Kleemann *et al.*, 2006). Amongst these applications, are antimycobacterial activities, as found for a series of *N*-(aryl)-2-thiophen-2-ylacetamide derivatives (Lourenço *et al.*, 2007), one structure of which, *i.e.* *N*-(2,6-dimethylphenyl)-2-(thiophen-2-yl)acetamide, was recently reported (Ferreira *et al.*, 2009). Herein, we now report the structure of the title compound (I) prepared by the controlled reaction of *p*-iodophenylhydrazine with 2,5-thiophenedicarbaldehyde. As indicated in the literature, controlled reactions of arylhydrazines with arenedicarbaldehydes can successfully produce mono-hydrazones (Reuch & Heflet, 1956; Vaysse & Pastour, 1964; Butler *et al.*, 1990; Glidewell, *et al.*, 2005; Low *et al.*, 2006; Wardell *et al.*, 2006).

The overall molecule of (I), Fig. 1, is non-planar as evidenced by the dihedral angle of 21.4 (3)° formed between the thiophene and benzene rings. The twist in the molecule is most evident in the C4–N1–N2–C7 torsion angle of -172.2 (6)° and, more particularly, in the adjacent N2–N1–C4–C3 torsion angle of -20.8 (9)°. The conformation about the C7=N2 bond [1.284 (8) Å] is *E*. The thiophene-S and aldehyde-O atoms are *syn* and are directed towards the benzene ring so that, overall, the molecule has a U-shape. The most prominent intermolecular interactions operating in the crystal structure are N–H⋯O hydrogen bonds, Table 1. These lead to supramolecular chains along the *b* direction, Fig. 2. Chains are connected along the *c* direction by I⋯I contacts [$I\cdots I^i = 3.7630(8)$ Å for *i*: -*x*, 1 - *y*, 1 - *z*] to form a 2-D array. Layers thus formed stack along the *a* direction, Fig. 3.

Experimental

A solution of *p*-iodophenylhydrazine (117 mg, 0.5 mmol) in MeOH (10 ml) was slowly added to a solution of 2,5-thiophenedicarbaldehyde (70 mg, 0.5 mmol) in MeOH (5 ml) at room temperature. The reaction mixture was maintained at room temperature and the crystals, which slowly formed, were collected and recrystallized from MeOH, m.pt. 464–467 K (dec.). IR(KBr, cm⁻¹): 1675 (C=O), 1593(C=N).

Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The N–H atom was located in a difference map and refined with the distance restraint N–H = 0.88±0.01 and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Figures

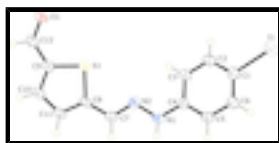


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

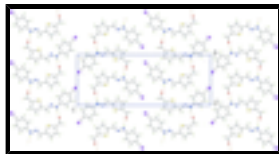


Fig. 2. A view of the supramolecular 2-D array in (I) mediated by N–H···O hydrogen bonding (orange dashed lines) leading to chains in the b direction held together in the c direction by I···I contacts (not illustrated). Colour code: I, pink; S, yellow; O, red; N, blue; C, grey; and H, green.

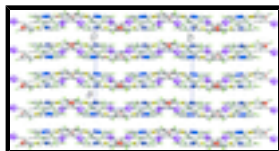


Fig. 3. A view of the stacking of layers (illustrated in Fig. 2) along the a direction in (I). Colour code: I, pink; S, yellow; O, red; N, blue; C, grey; and H, green.

5-[[*(E)*-2-(4-Iodophenyl)hydrazinylidene]methyl]thiophene-2-carbaldehyde

Crystal data

C₁₂H₉IN₂OS

M_r = 356.17

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

a = 6.9291 (9) Å

b = 11.7602 (10) Å

c = 30.958 (4) Å

V = 2522.7 (5) Å³

Z = 8

F(000) = 1376

D_x = 1.876 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 16555 reflections

θ = 2.9–27.5°

μ = 2.69 mm⁻¹

T = 120 K

Prism, colourless

0.16 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: Enraf Nonius FR591 rotating anode

10 cm confocal mirrors

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2007)

T_{min} = 0.616, *T_{max}* = 0.746

15735 measured reflections

2614 independent reflections

1674 reflections with *I* > 2σ(*I*)

R_{int} = 0.095

θ_{max} = 26.5°, θ_{min} = 3.2°

h = -8→8

k = -14→14

l = -38→37

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.058

wR(*F*²) = 0.113

S = 1.04

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0257*P*)² + 17.1487*P*]

2614 reflections
157 parameters
1 restraint

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 1.08 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	-0.01127 (8)	0.34335 (4)	0.487908 (18)	0.04277 (19)
S1	0.1013 (3)	0.10271 (14)	0.21597 (6)	0.0261 (4)
N1	0.0936 (8)	-0.0324 (5)	0.3466 (2)	0.0282 (14)
H1N	0.039 (9)	-0.099 (3)	0.350 (2)	0.034*
N2	0.1043 (8)	0.0033 (5)	0.3048 (2)	0.0266 (13)
O1	0.1012 (7)	0.2541 (4)	0.13359 (16)	0.0336 (12)
C1	0.0410 (10)	0.2143 (6)	0.4423 (2)	0.0323 (18)
C2	0.1194 (10)	0.2425 (6)	0.4030 (2)	0.0322 (18)
H2	0.1610	0.3182	0.3976	0.039*
C3	0.1374 (9)	0.1609 (6)	0.3714 (2)	0.0278 (16)
H3	0.1900	0.1808	0.3441	0.033*
C4	0.0794 (9)	0.0499 (6)	0.3792 (2)	0.0231 (15)
C5	0.0110 (10)	0.0198 (5)	0.4197 (2)	0.0284 (16)
H5	-0.0202	-0.0573	0.4257	0.034*
C6	-0.0121 (10)	0.1017 (6)	0.4514 (2)	0.0332 (17)
H6	-0.0631	0.0820	0.4789	0.040*
C7	0.0949 (10)	-0.0729 (6)	0.2752 (2)	0.0275 (17)
H7	0.0837	-0.1509	0.2827	0.033*
C8	0.1016 (9)	-0.0394 (5)	0.2306 (2)	0.0249 (16)
C9	0.1085 (9)	0.0672 (6)	0.1616 (2)	0.0239 (15)
C10	0.1118 (10)	-0.0491 (6)	0.1562 (2)	0.0291 (17)
H10	0.1177	-0.0849	0.1288	0.035*
C11	0.1057 (10)	-0.1090 (6)	0.1951 (2)	0.0292 (16)
H11	0.1046	-0.1897	0.1968	0.035*
C12	0.1088 (9)	0.1509 (6)	0.1282 (2)	0.0288 (16)
H12	0.1156	0.1243	0.0993	0.035*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0425 (3)	0.0365 (3)	0.0493 (3)	-0.0005 (3)	0.0024 (3)	-0.0128 (3)
S1	0.0228 (9)	0.0219 (8)	0.0336 (10)	-0.0006 (8)	0.0004 (8)	-0.0049 (8)
N1	0.023 (3)	0.020 (3)	0.042 (4)	-0.002 (3)	0.004 (3)	0.001 (3)
N2	0.020 (3)	0.030 (3)	0.030 (4)	0.001 (3)	0.005 (3)	0.003 (3)
O1	0.027 (3)	0.025 (3)	0.049 (3)	-0.003 (2)	-0.004 (3)	-0.001 (2)
C1	0.029 (4)	0.033 (4)	0.035 (4)	0.001 (3)	-0.007 (3)	-0.003 (3)
C2	0.025 (4)	0.027 (4)	0.045 (5)	-0.005 (3)	-0.005 (4)	-0.002 (3)
C3	0.018 (3)	0.026 (4)	0.039 (4)	-0.002 (3)	-0.002 (3)	-0.001 (3)
C4	0.018 (3)	0.024 (4)	0.027 (4)	0.001 (3)	-0.002 (3)	-0.001 (3)
C5	0.027 (4)	0.020 (3)	0.038 (4)	0.001 (3)	-0.003 (4)	0.003 (3)
C6	0.034 (4)	0.032 (4)	0.034 (4)	0.002 (4)	0.001 (4)	-0.001 (3)
C7	0.021 (4)	0.022 (4)	0.040 (5)	0.000 (3)	0.000 (4)	0.001 (3)
C8	0.017 (3)	0.018 (3)	0.039 (4)	-0.002 (3)	0.001 (3)	-0.005 (3)
C9	0.012 (3)	0.031 (4)	0.029 (4)	0.002 (3)	0.001 (3)	-0.006 (3)
C10	0.023 (4)	0.025 (4)	0.039 (5)	0.001 (3)	-0.002 (3)	-0.011 (3)
C11	0.026 (4)	0.018 (3)	0.044 (5)	0.000 (3)	0.010 (4)	-0.006 (3)
C12	0.020 (3)	0.027 (4)	0.040 (5)	0.005 (4)	-0.002 (3)	-0.007 (3)

Geometric parameters (\AA , $^\circ$)

I1—C1	2.103 (7)	C4—C5	1.387 (9)
S1—C8	1.732 (7)	C5—C6	1.386 (9)
S1—C9	1.734 (7)	C5—H5	0.9500
N1—N2	1.362 (8)	C6—H6	0.9500
N1—C4	1.402 (8)	C7—C8	1.436 (9)
N1—H1N	0.876 (10)	C7—H7	0.9500
N2—C7	1.284 (8)	C8—C11	1.371 (9)
O1—C12	1.227 (8)	C9—C10	1.378 (9)
C1—C2	1.374 (10)	C9—C12	1.429 (9)
C1—C6	1.403 (10)	C10—C11	1.395 (10)
C2—C3	1.376 (9)	C10—H10	0.9500
C2—H2	0.9500	C11—H11	0.9500
C3—C4	1.388 (9)	C12—H12	0.9500
C3—H3	0.9500		
C8—S1—C9	91.2 (3)	C5—C6—H6	120.5
N2—N1—C4	118.3 (6)	C1—C6—H6	120.5
N2—N1—H1N	114 (5)	N2—C7—C8	119.6 (6)
C4—N1—H1N	120 (5)	N2—C7—H7	120.2
C7—N2—N1	117.4 (6)	C8—C7—H7	120.2
C2—C1—C6	120.6 (7)	C11—C8—C7	127.4 (6)
C2—C1—I1	119.2 (5)	C11—C8—S1	111.5 (5)
C6—C1—I1	120.1 (5)	C7—C8—S1	121.1 (5)
C1—C2—C3	119.8 (7)	C10—C9—C12	126.6 (6)
C1—C2—H2	120.1	C10—C9—S1	110.9 (5)

C3—C2—H2	120.1	C12—C9—S1	122.5 (5)
C2—C3—C4	120.5 (7)	C9—C10—C11	113.3 (6)
C2—C3—H3	119.8	C9—C10—H10	123.3
C4—C3—H3	119.8	C11—C10—H10	123.3
C3—C4—C5	119.7 (6)	C8—C11—C10	113.0 (6)
C3—C4—N1	120.4 (6)	C8—C11—H11	123.5
C5—C4—N1	119.9 (6)	C10—C11—H11	123.5
C6—C5—C4	120.2 (6)	O1—C12—C9	125.7 (7)
C6—C5—H5	119.9	O1—C12—H12	117.2
C4—C5—H5	119.9	C9—C12—H12	117.2
C5—C6—C1	118.9 (7)		
C4—N1—N2—C7	-172.2 (6)	N2—C7—C8—C11	175.5 (7)
C6—C1—C2—C3	3.2 (11)	N2—C7—C8—S1	-5.6 (9)
I1—C1—C2—C3	-173.9 (5)	C9—S1—C8—C11	-0.4 (5)
C1—C2—C3—C4	-0.9 (10)	C9—S1—C8—C7	-179.4 (6)
C2—C3—C4—C5	-3.0 (10)	C8—S1—C9—C10	-0.3 (5)
C2—C3—C4—N1	178.4 (6)	C8—S1—C9—C12	179.2 (6)
N2—N1—C4—C3	-20.8 (9)	C12—C9—C10—C11	-178.5 (6)
N2—N1—C4—C5	160.6 (6)	S1—C9—C10—C11	0.9 (8)
C3—C4—C5—C6	4.5 (10)	C7—C8—C11—C10	180.0 (7)
N1—C4—C5—C6	-176.9 (6)	S1—C8—C11—C10	1.0 (8)
C4—C5—C6—C1	-2.1 (11)	C9—C10—C11—C8	-1.2 (9)
C2—C1—C6—C5	-1.7 (11)	C10—C9—C12—O1	178.2 (7)
I1—C1—C6—C5	175.4 (5)	S1—C9—C12—O1	-1.2 (10)
N1—N2—C7—C8	178.7 (6)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1n\cdots O1^i$	0.88 (4)	2.05 (5)	2.916 (8)	172 (5)

Symmetry codes: (i) $-x, y-1/2, -z+1/2$.

Fig. 1

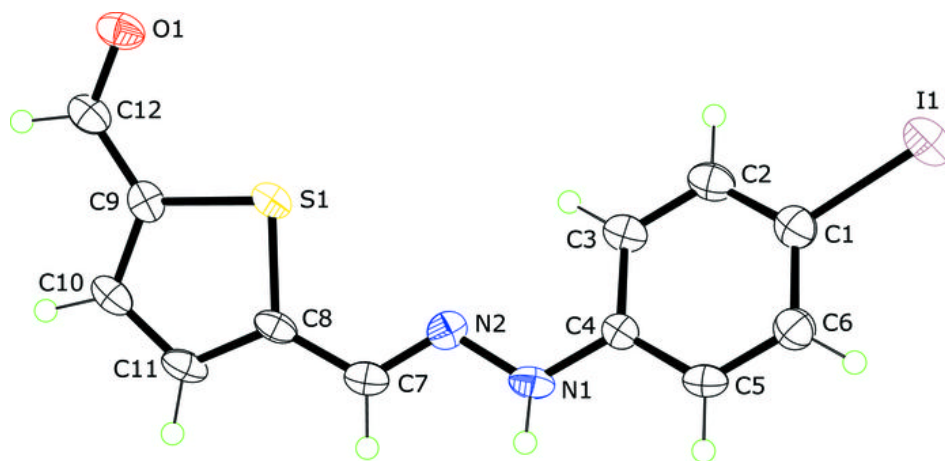


Fig. 2

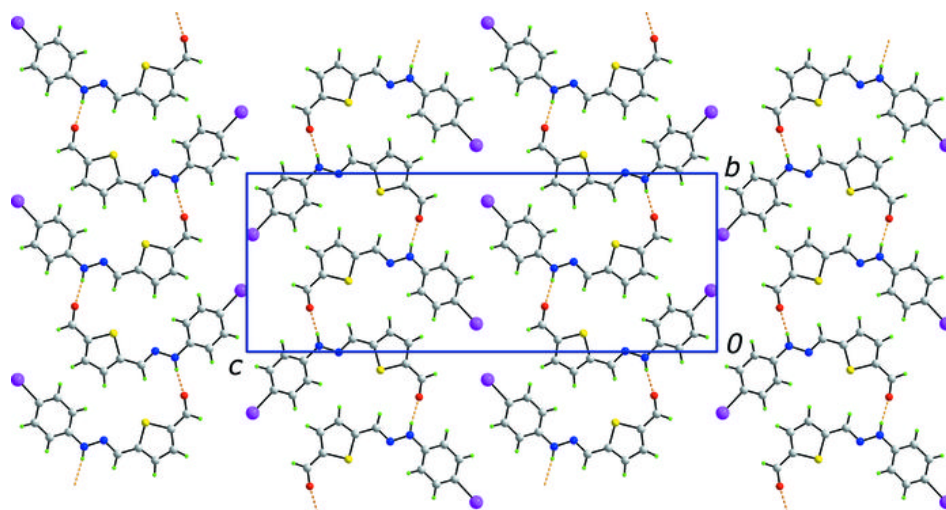


Fig. 3

